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EFFECT OF ELECTRON DETACHMENT ON THE WALL POTENTIAL AND PLASMA EVOLUTION IN THE AFTERGLOW STAGE (Postprint)

E.A. Bogdanov, C.A. DeJoseph Jr., V.I. Demidov, and A.A. Kudryavtsev

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6. AUTHOR(S)
E.A. Bogdanov and A.A. Kudryavtsev (St. Petersburg State University)
C.A. DeJoseph Jr. (Electrical Technology and Plasma Physics Branch (AFRL/PRPE))
V.I. Demidov (UES, Inc.)

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14. ABSTRACT
It is demonstrated that detachment of electrons in the afterglow of an electronegative plasma can lead to a significant increase in negative wall potential with respect to the plasma potential. This effect can be used to modify the near-wall sheath electric field and thickness, which are important for plasma processing applications. Also in the afterglow, this effect can lead to an increase in electron density with time, and a reduction (up to total exclusion) in diffusion cooling of electrons and can thus be used to modify the electron temperature.

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Effect of electron detachment on the wall potential and plasma evolution in the afterglow stage

E. A. Bogdanov
St. Petersburg State University, St. Petersburg 198904, Russia

C. A. DeJoseph, Jr.
Air Force Research Laboratory, Wright-Patterson AFB, Dayton, OH 45433

V. I. Demidov
UES, INC., 4401 Dayton-Xenia Rd., Dayton, OH 45432

A. A. Kudryavtsev
Department of Optics and Spectroscopy, St. Petersburg State University, St. Petersburg 198904, Russia

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It is demonstrated that detachment of electrons in the afterglow of an electronegative plasma can lead to a significant increase in negative wall potential with respect to the plasma potential. This effect can be used to modify the near-wall sheath electric field and thickness, which are important for plasma processing applications. Also in the afterglow, this effect can lead to an increase in electron density with time, and a reduction (up to total exclusion)in diffusion cooling of electrons and can thus be used to modify the electron temperature.

The use of pulse discharges in various research and industry applications allows a wider range of plasma properties and, therefore, more options for improving both the quality and scope of plasma assisted fabrication [1, 2]. These discharges also allow for the possibility of developing methods for controlling various plasma parameters, based on the non-local nature of the electron energy distribution function (EEDF) in low-pressure plasmas [3, 4]. In such a plasma the electron energy relaxation length λ_ε typically exceeds the characteristic dimension of the plasma volume L and the EEDF is non-local (see, [5] for details). When this occurs, the electron kinetics cannot be described by the fluid approximation and the form of the EEDF can vary spatially over the discharge volume. If m and v are the electron mass and velocity and φ is the plasma potential at a point $\vec{r}$, then electrons with energy $\varepsilon = mv^2/2 + e\varphi(\vec{r})$, which is less than $e\Phi_w$, where Φ_w is the wall potential, are trapped in the plasma volume and cannot contribute to electron current to the walls. Thus, the current in the vicinity of a surface is transported in the form of free diffusive flux of fast untrapped (free) electrons.

Since the number of these higher energy, free electrons is always small, the addition to the plasma of even a small number of fast electrons (say, $10^{-5}N_e$, where N_e is the total density of electrons) with energies $\varepsilon_f \gg T_e$ can dramatically increase both the thickness and potential of the sheath [3]. Such an effect was been experimentally observed in Ar pulsed radio-frequency (rf) inductively coupled plasma (ICP) sources [6] and was linked with the creation of fast electrons in Penning and superelastic collisions involving noble gas metastable atoms. In molecular and electronegative gases the density of excited or active molecules are typically high [7]. As a result, it is reasonable to expect that effects connected with the creation of fast electrons will exist and can be used for industrial applications. In this paper we discuss some possible scenarios which result in an anomalous near-wall sheath in the afterglow plasma of an electronegative gas. Specifically, we describe a numerical simulation of an oxygen discharge in a specific discharge geometry, which allows us to confirm that these effects can be important in the plasma.

Let us briefly discuss reasons for a significant change in the afterglow near-wall sheath potential as a result of the presence of even a small number of fast electrons. In an oxygen plasma, these fast electrons can arise from the associative detachment reaction involving O^- negative ions and atomic oxygen,

$$O^- + O \rightarrow O_2 + e_f \qquad (1)$$

where e_f represents a fast electron with energy $\varepsilon_f = 3.6$ eV. For brevity we will call electrons produced in reaction (1) as the "fast group". This energy is much higher than the typical electron temperature in the afterglow (~ 0.1 eV). Higher energy electrons from the bulk will simply be referred to as "hot electrons". During the active phase of the discharge $e\Phi_w$ is typically greater than the energy of the fast group, (during this phase their energy is on the order of the electron temperature). As a result these electrons are trapped in the plasma volume and do not contribute to the electron flux to the walls. At low pressures (volume recobination processes can be neglected) and for the quasistationary case during the active phase, the rate of ionization of oxygen is equal to the flux of ions to the wall due to ambipolar diffusion (Γ_a). At the same time, the rate of electron attachment (Γ_{atch}) is equal to the rate of their detachment (Γ_{det}). The ratio of ionization rate to detachment rate will, in general, depend on the gas pressure.

Following termination of the discharge, T_e decreases rapidly and after a time of order of a few tens of microseconds becomes of order of 0.1 eV. For this temperature, the ionization rate from electron impact becomes very small and can be neglected. Likewise, the potential drop inside the plasma as a result of ambipolar diffusion becomes small compared to the energy of the fast group. Under these conditions, the fast group free to diffuse to the plasma wall and, if the pressure is high enough (but still low enough to neglect volume recombination processes) to further reduce ambipolar diffusion, their flux to the walls can be significantly higher than the ambipolar ion flux. At very low pressures the fast group flux is reduced due to decreased O^- density and ambipolar diffusion is large enough so that the fast group does not significantly contribute to the electron flux to the walls and charge balance is primarily between ions and hot electrons. At intermediate pressures, the situation can become more complex. At the beginning of the afterglow, the ambipolar ion flux will likely exceed the fast group flux and will be balanced by the residual hot electrons remaining from the active phase. However, at some later time, due to the rapidly decreasing T_e, the ambipolar ion flux may become smaller than the flux from the fast group and this situation may exist for some time. If at any time the flux of fast electrons exceeds the ambipolar ion flux, to maintain quasineutrality a part of the detached electrons must also be trapped in the plasma volume by the increased (close to the energy of the fast group) wall potential. In this case all thermal electrons and a portion of the fast group will be trapped in the plasma volume, which can lead to an increase in electron density during the afterglow. It was shown (see, [3] for details) that a very small relative density of fast electrons is sufficient to create this situation. In that work, fast electrons were generated by reactions of metastable atoms. For that case, effect similar to those in the low and itermediate pressue situations described above are seen. Effects similar to the higher pressure situation described above are not seen in these rare gase plasmas [3]. This effect can, therefore, be used to control the near-wall sheath electric field and thickness, which are important for plasma-processing applications. This effect also leads to an increasing electron density with time in the afterglow, decreasing (up to completely eliminating) the diffusion cooling of electrons and can be used to control the electron temperature.

To confirm the above qualitative arguments, simulations on a pulsed (100% modulated) rf ICP were conducted for the discharge system described in Ref. [8]. This system is composed of two concentric cyclinders, a small (0.8 liter) "discharge chamber" located at one end of a much larger (350 liters) "vacuum chamber". The rf window is located on the back end of the discharge chamber while the opposite end is open. The plasma is initiated at the rf window and freely expands into the vacuum chamber. This system was chosen since it had been characterized in earlier modeling in argon (unpub-

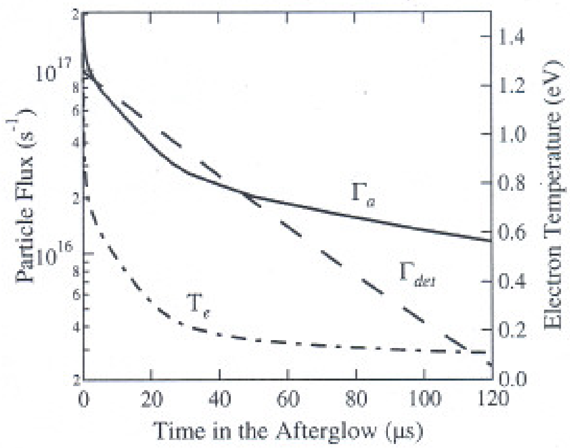

FIG. 1: Calculated ambipolar ion flux, Γ_a, detachment flux, Γ_{det} from reaction (1), shown on the left axis, and the bulk electron temperature, T_e, shown on the right axis.

lished). The discharge was simulated using a commercial software package [9] with modifications. A detailed self-consistent model of the discharge plasma, numerical iteration scheme, and technique for solving the set of equations are described in [9]. The density and mean energy of the electron component can be obtained by solving either the fluid balance equations or the kinetic equations for the EEDF. The self-consistent electric field is found from Poissons equation. Heavy particles are described using the fluid model. The list of plasmachemical reactions used can be found in [10]. We solve the balance equations for the two lowest vibrational levels of the ground electronic state, $O_2(X^3\Sigma_g^-(v=0,1))$, and the electronically-excited states $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, and $O_2(Ry)$); the atomic states $O(^3P)$, $O(^1S)$, $O(^1D)$; the ozone molecule, O_3; and the ions O^+, O_2^+ , O_4^+ , O^- , O_2^-, and O_3^-, with a total of 160 plasmochemical reactions between them. The simulations were conducted over a range of values of the rf power, but all of the data shown were calculated for an rf power of 25 W. The active phase of the discharge had a duration of 100 μs and a repetition frequency of 1.6 kHz. Pressure for the simulations was set at 20 mTorr, which is a typical operating pressure for the device. In Figs. 1-3 results of the simulations with selected plasma parameters and fluxes are shown. Fig. 1 shows the calculated ambipolar ion flux and the flux of the fast group from detachment. Also shown on the right axis of Fig. 1 is T_e of the bulk. At t=0, T_e is approximately 4 eV but falls rapidly until it reaches $\sim$ 0.1 eV at 120 μs. Fig. 1 shows that during the time between 3 and 45 μs the flux from detachment (fast group) exceeds the ambipolar ion flux. This should lead to trapping of all thermal electrons and a portion of the fast group during this part of the afterglow. This picture corresponds to the intermediate pressure regime qualitatively described earlier. Fig. 2 shows the charged particle densities in the afterglow

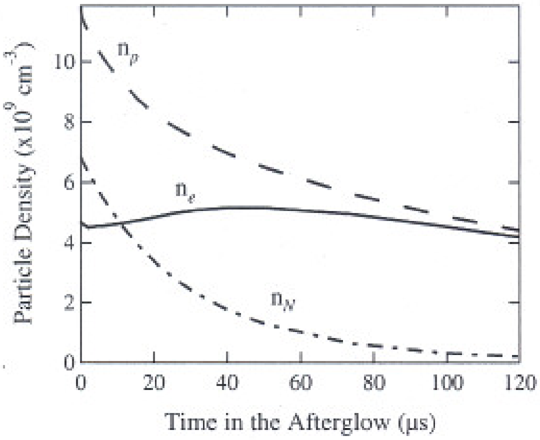

FIG. 2: Calculated charged particle densities in the afterglow. Electron density, n_e, negative ion density, n_N, and positive ione density, n_p are shown.

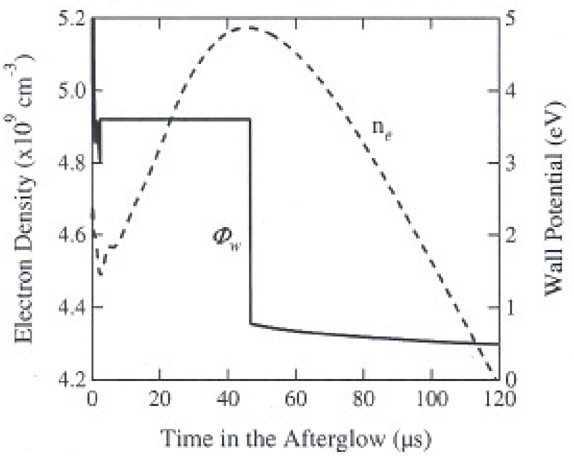

FIG. 3: Detail of electron density, n_e, on the left axis and the calculated wall potential, Φ_w on the right axis.

over the same time period as Fig. 1. As can be seen, both positive and negative ion densities decrease monotonically in the afterglow, as might be expected from diffusion losses. On the other hand, n_e is seen to initially decrease, then increase for a time between 3 and 45 μs, and then decrease again. This increase corresponds to the time interval when electrons are trapped by the high wall potential. To further illustrate this point, Fig. 3 shows detail of n_e along with the calculated wall potential, Φ_w. It is clear in this figure that n_e begins to increase as Φ_w increases and climbs until Φ_w drops. This drop corresponds to the point when Γ_a becomes less than Γ_{det}. Without the presence of the fast group, one would normanly expect the wall potential to monotonically decrease as T_e does in Fig. 1. The calculations clearly show the effects of the fast group on the wall potential.

In this paper we have shown that in the afterglow of an electronegative plasma, electron detachment can lead to such paradoxical phenomena as a sharp increase in the potential drop in the near-wall sheath (during a time when the electron temperature is decreasing), an increase in the electron density and a reduction (up to total exclusion) of diffusion cooling, which strongly effects the electron temperature in these low-pressure plasmas. These phenomena can be used to modify the plasma and near-wall sheath properties, and the electron temperature for improving plasma processing and the efficiency of various plasma devices.

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